

Engine Friction Reduction - Part II

(Base fluid and additive technologies)

O. O. Ajayi, C. Lorenzo-Martin, D. Singh,
A. Erdemir, and G. R. Fenske

Argonne National Laboratory

2015 Annual Merit Review

June 9, 2015

Project ID # ft029

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Project start date FY 13
- Project end date FY 19
- Percent complete 40%

Budget

- FY 14 Project Funding \$1838K
 - DOE Share \$1588K
 - Contractor Share* \$250K
- FY 15 \$970K

* CRADA in-kind and funds-in contributions

Barriers

- Fuel economy improvement via lubricants and tribology
- Reduction of greenhouse gas (GHG) emissions
- Reliability/durability
 - Impact of lubes on after-treatment devices
 - Lube compatibility with alternative fuels
 - Lubricating alternative (non-traditional) materials
 - Alternative lube stocks (bio-based)

Partners

- MIT – Lube Consortium
- Vehicle and Engine OEMS
- Component OEMs
- Lubricant Suppliers
- Additive Suppliers
- Small Businesses, Academia



Tasks Objective and Relevance

- **Objective:** Develop base oil and additive technologies to reduce friction in all lubrication regimes without compromising reliability and durability.

- **Relevance:** Various lubricated engine components and systems operate in different lubrication regimes. Sustainable engine friction reduction to enable increased efficiency in all lubrication regimes.
 - Hydrodynamic regime friction dependent largely on base oil viscosity.
 - Mixed and boundary regime friction governed by additives.
 - Lubricant technology is the only viable drop-in approach for legacy vehicles
 - Advanced base oil may enable use of less additives.



Project Focus and Expected Outcome

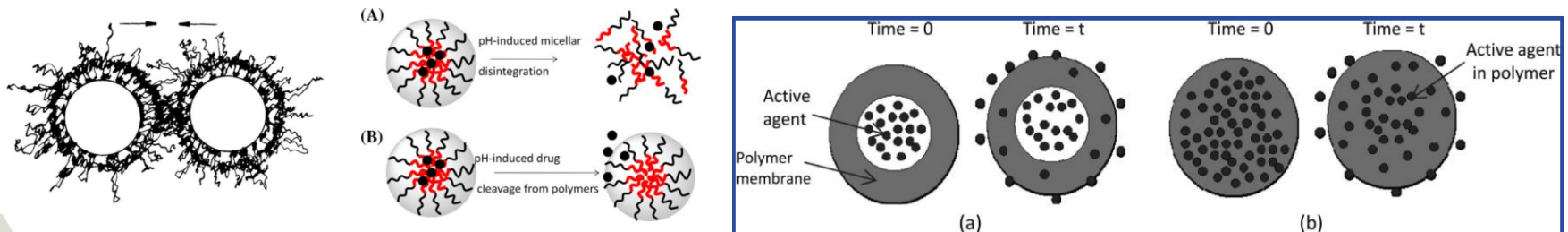
- Engine lubricants consist of base oil and tribology performance functional additives.
 - Reducing the viscosity of base oil, will result in fluid film lubrication friction reduction.
 - Anti-wear, friction modifier and extreme pressure additives will reduce friction and protect surfaces under boundary regime.
- The project will focus on the development of ultra-low viscosity base oil to reduce fluid film lubrication friction under hydrodynamic and EHD regimes.
- The additives component of the project will focus on the development of functional additive systems applicable to all materials.

Technical Approach/Strategy - base oil

- There are synthetic base oil currently used for very challenging applications because of some desirable properties:
 - Stability over a wide temperature range.
 - Low volatility.
 - Inherent lubricity and wear protection attributes.
 - Available in wide range of viscosities.
- PAO- and Ester-based fluids meet these requirements.
- Develop composite base fluids consisting of very low viscosity components from PAO and Ester chemistries.
 - Optimize fluid mixture using thermodynamics principles
 - Characterize the rheological properties of fluid mixture
 - Evaluate tribological performance of composite base fluids
 - Determine the impact of additives on the tribological performance of new composite base fluid.

Technical Approach -Additives

- Current state-of-the-art lubricant additives performs several tribological functions via *surface chemical reactions*
 - Friction control (FM); wear prevention (AW); scuffing prevention (EP); chemical stability (AO); thermal dissipation
 - Often specific to ferrous surface and limited effectiveness
- New advanced lubricant additives based on *physical and/or chemical mechanisms* using colloidal additive technology to provide appropriate tribological attributes – can be used with different materials including coatings
 - Friction reducing particles – layer nano particles (MoS_2 , h-BN, Graphite, Cu Ag.....)
 - Wear and scuffing performance – oxides and metallic nano particles (TiO_2 , SiO_2 , Ag, Cu,)
 - Chemical stability - (CaCO_3 , $\text{Mg}(\text{OH})_2$,)
 - Thermal dissipation – high conductivity nano particles (Cu, Ag, C,)
- Time control release attributes will be achieved by encapsulating the nano additives in an appropriate shell or surface layer – similar to pharmaceutical drug formulation



Technical Approach - additives

- Comprehensive tribological performance evaluation of Advanced current state-of-the-art commercial engine lubricants – performance benchmark for the project
 - Frictional attributes under different lubrication regimes
 - Wear behavior under different contact conditions
 - Scuffing performance under severe contact conditions
- Identify, design and synthesis of encapsulated colloidal particulate additive systems with desired tribological performance attributes: Friction reduction, wear protection and scuffing prevention
- Comprehensive tribological performance of candidate systems for various attributes
 - Effect of concentration
 - Combination of additives
- Mechanistic studies of candidate additives.
 - Optimization of the additive and base-fluid systems
- Technology transfer to appropriate stakeholders.

FY14 and FY15 Project Milestones

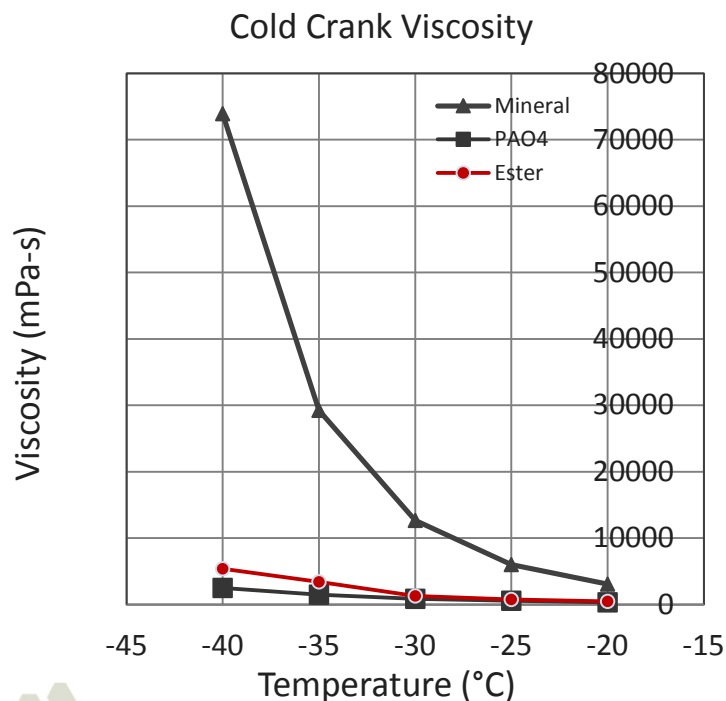
Month/Year	Milestone
03/15	Complete rheological properties characterization of composite fluid mixtures (completed)
06/15	Complete preliminary friction and wear performance evaluation of composite base fluid under unidirectional and reciprocating sliding (complete)
03/15	Characterize colloidal particulate additive candidate. (completed)
09/15	Complete initial tribological performance evaluation of some candidate colloidal additive systems as proof of concept (On going)

Technical Accomplishment and Progress:-measurement of fluid mixture viscosity

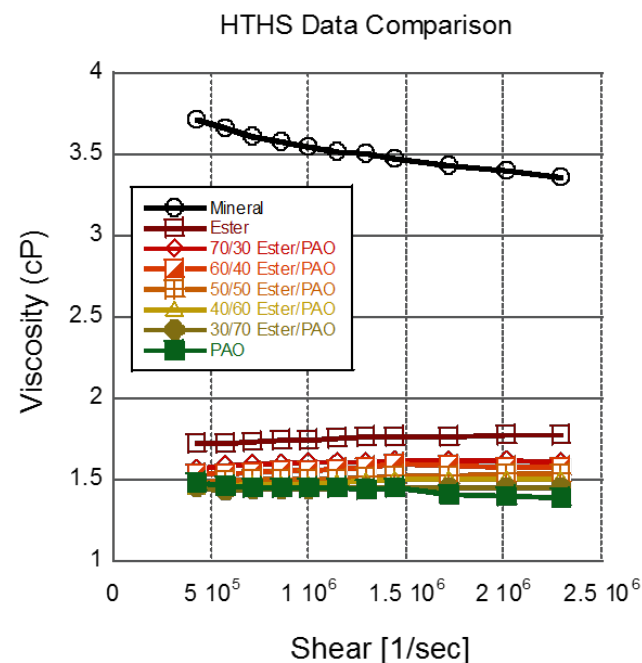
Note: Percentages by volume

100% PAO4
70% PAO4, 30% Ester
60% PAO4, 40% Ester
50% PAO4, 50% Ester
40% PAO4, 60% Ester
30% PAO4, 70% Ester
100% Ester

%Ester ratio	Kinematic Viscosity (cSt)			Cold Crank Viscosity (cP)				
	40°C	100°C	VI	-20°C	-25°C	-30°C	-35°C	-40°C
0	17.8	4	124	306	563	846	1453	2489
30	17.8	4.06	130	319	572	862	1490	2575
40	17.9	3.95	117	302	572	866	1511	2635
50	17.9	4.01	123	331	601	925	1588	2784
60	18.3	4.16	133	337	609	928	1630	2874
70	18.4	4.34	150	350	639	994	1722	3060
100	19.6	4.33	132	439	770	1219	3414	5410



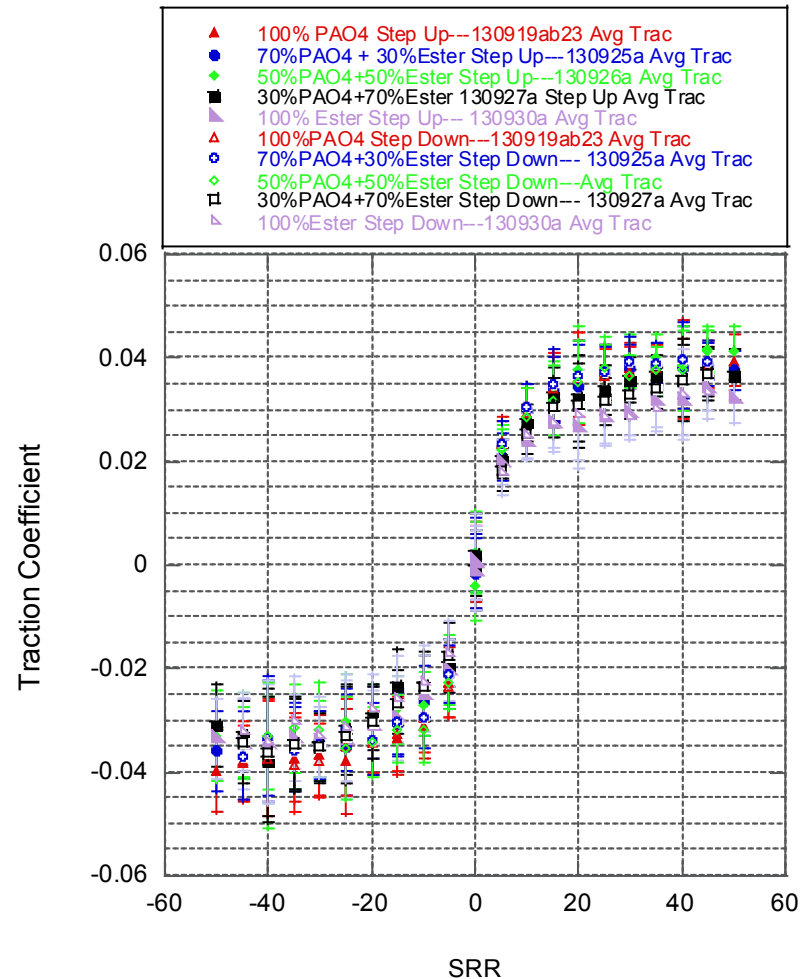
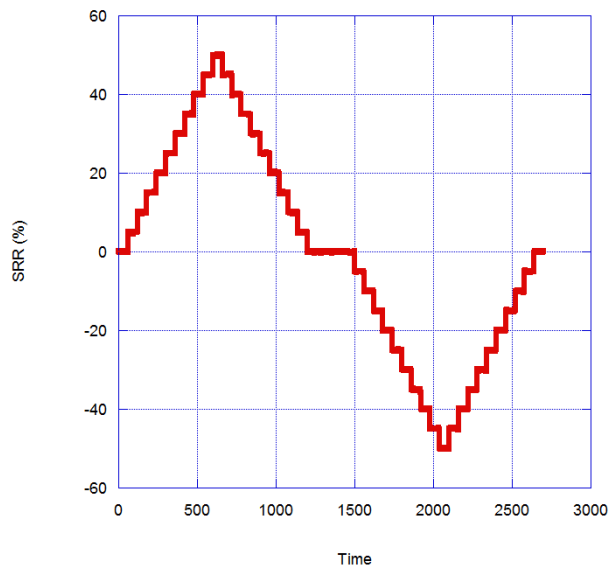
Thermodynamics based Rheological properties predictive model under development.
- General applicability to any fluid mixture including fuel-oil mixture



Technical Accomplishment and Progress:- Traction Test

TEST CONDITIONS

Rings	16crmn5-polished
Roller	16crmn5-polished
Oil	100%PAO4 70%PAO4+30%Ester 50%PAO4+50%Ester 30%PAO4+70%Ester 100%Ester
Speed	3.2 m/s
Load	100N
SRR	Range of -50% to 50%
Test Length	45 min
Temperature	Heated to 40C for first step then heater turned off
Data Logging Interval	1 sec

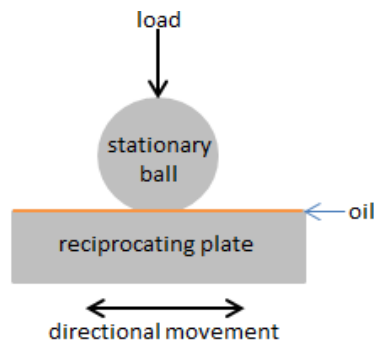


Significant traction (viscous losses) reduction in mixed fluids



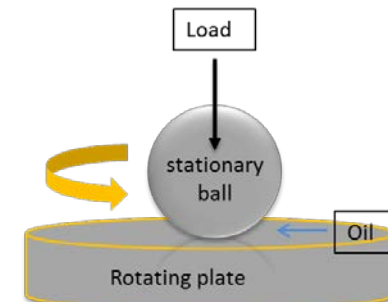
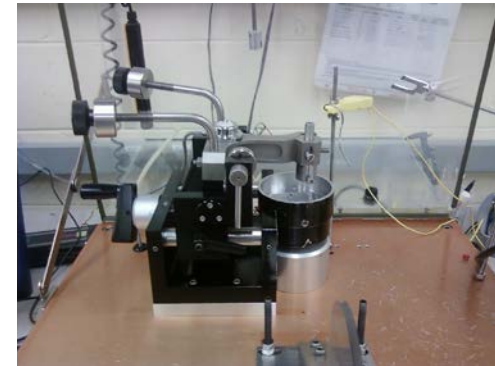
Preliminary Friction and Wear Performance Evaluation

Reciprocating sliding - HFRR test



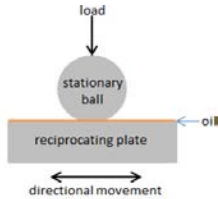
- Load: **15N** $\sigma_{max}=0.99$ GPa.
- Speed: 1cm/s (60 minutes) and variable: speed ramps-first and last 12 min: 0.1, 0.5, 1, 5, 10, 20 cm/s)
- Diameter: **12-16 mm**
- Duration: **84 minutes**
- Temperature: **100°C**

UNIDIRECTIONAL SLIDING - POD TEST

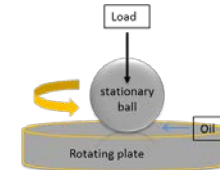
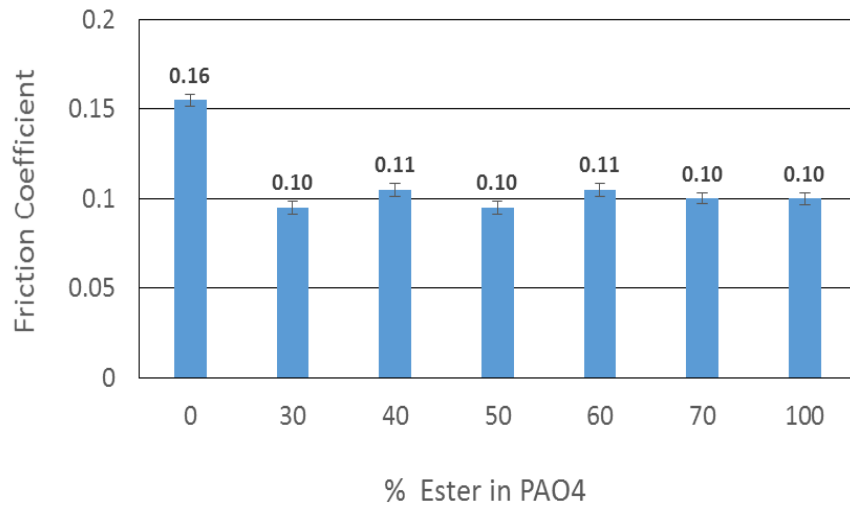


- Load: **15N** $\sigma_{max}=0.99$ GPa.
- Speed: **60rpm** (60 minutes) and 2 min variable speed ramps from **0-300 rpm** at the beginning and end of test.
- Stroke length: **10 mm**
- Duration: **64 minutes**
- Temperature: **100°C**

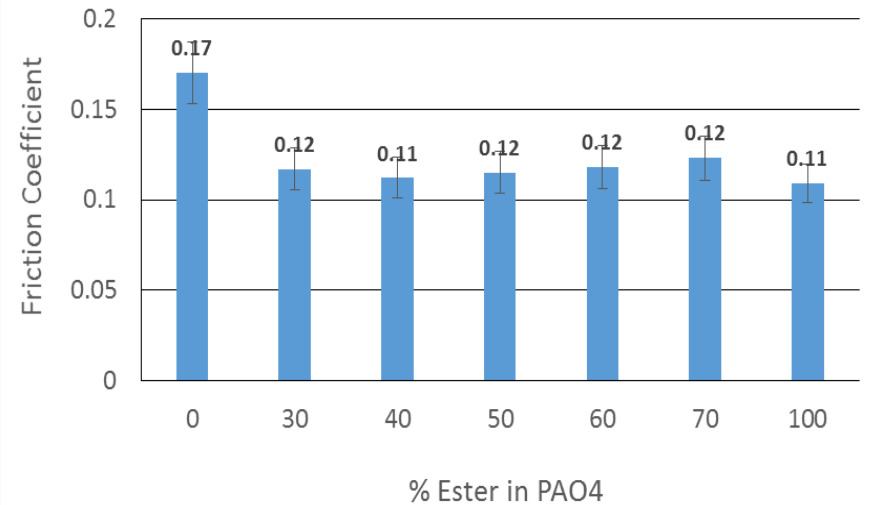
Friction Results



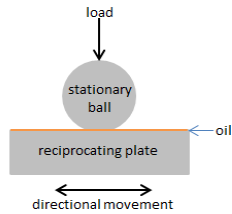
Reciprocating Sliding



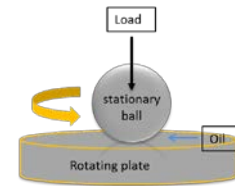
Unidirectional Sliding



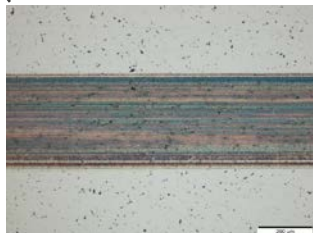
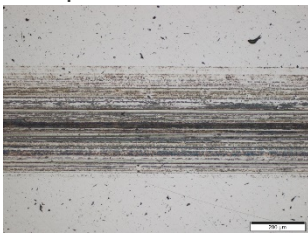
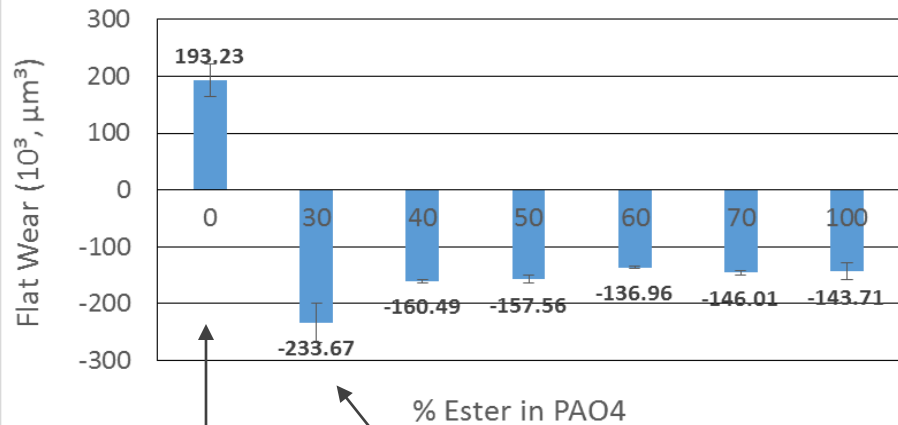
Flat Wear Results



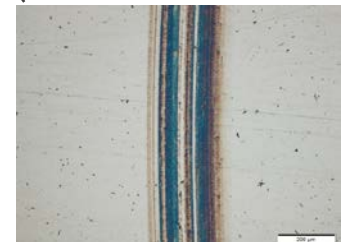
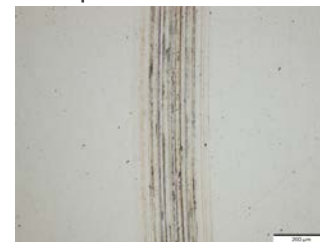
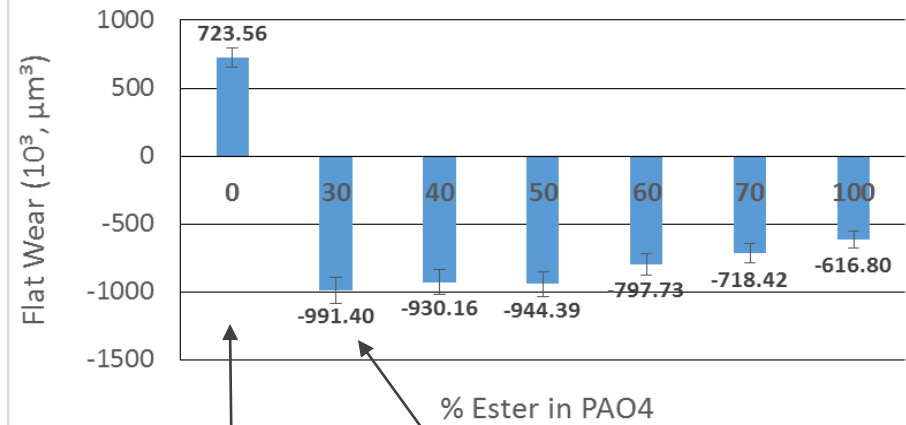
Surface protection against wear in fluid mixture – implication for anti-wear additives requirement



Reciprocating Sliding

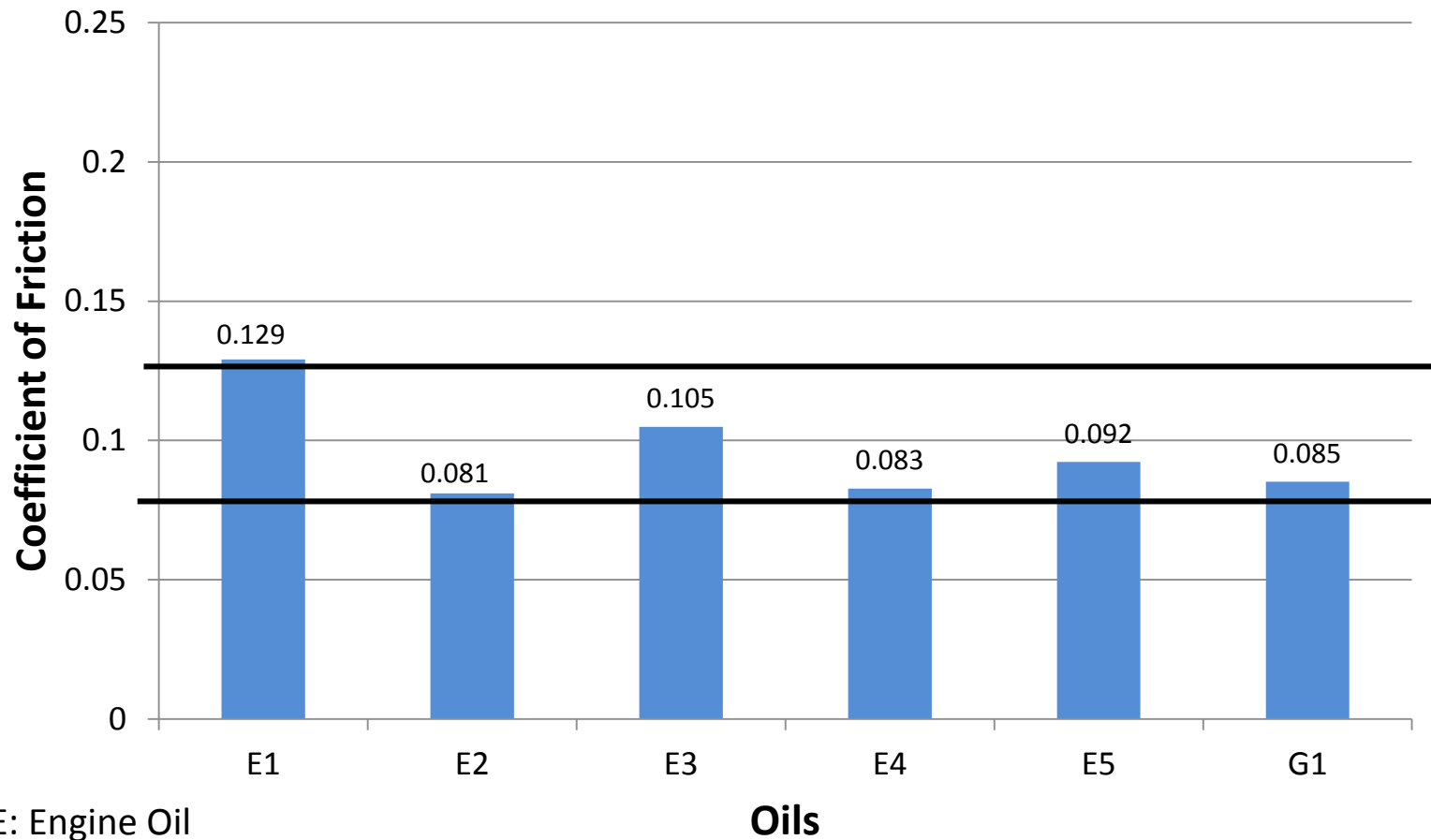


Unidirectional Sliding

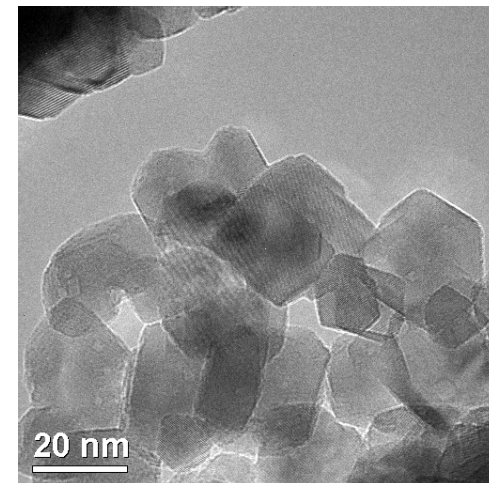
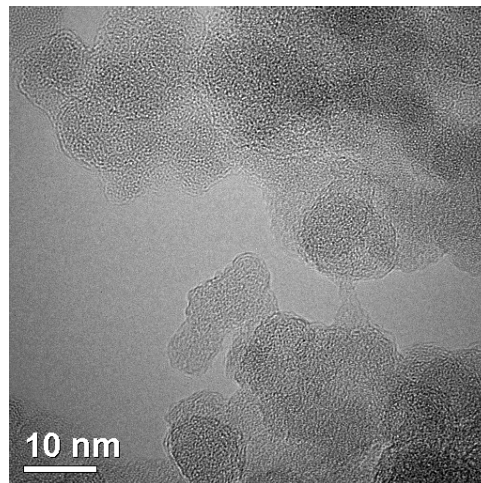
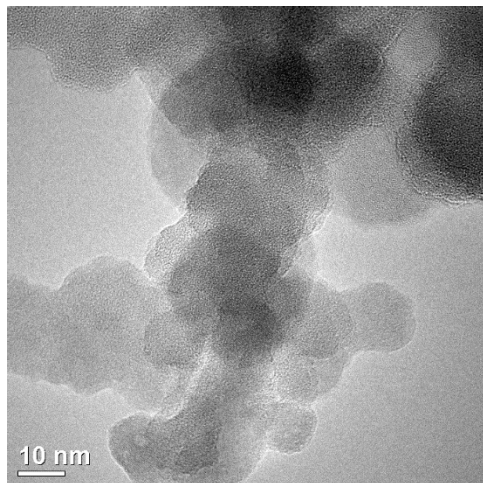


Technical Accomplishment and Progress: - Performance benchmark for new additive systems

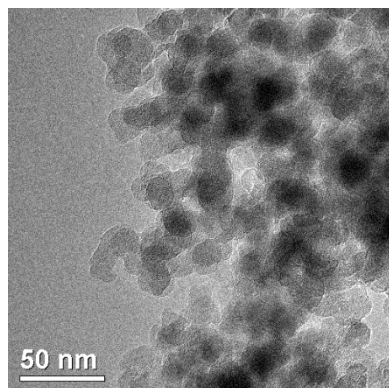
- Established benchtop tribological performance benchmark for the project
 - Measured various performance attributes for several advanced state-of-art lubricants



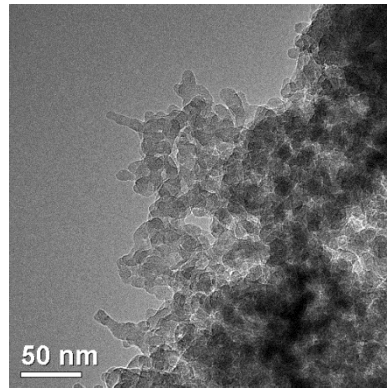
TEM- characterization colloidal particles



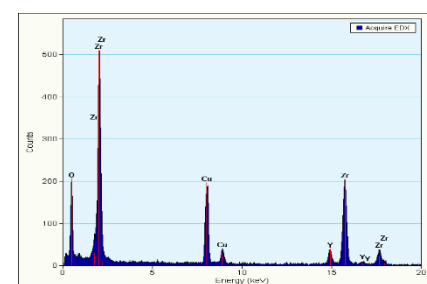
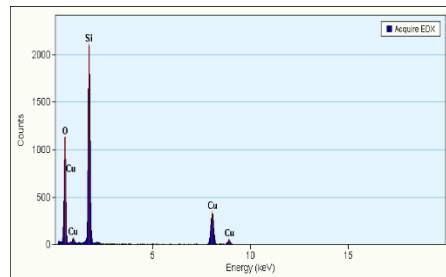
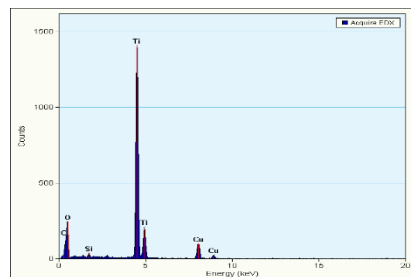
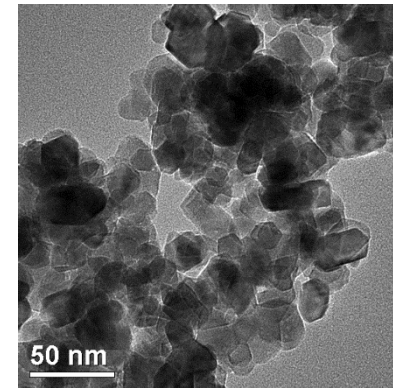
TiO₂



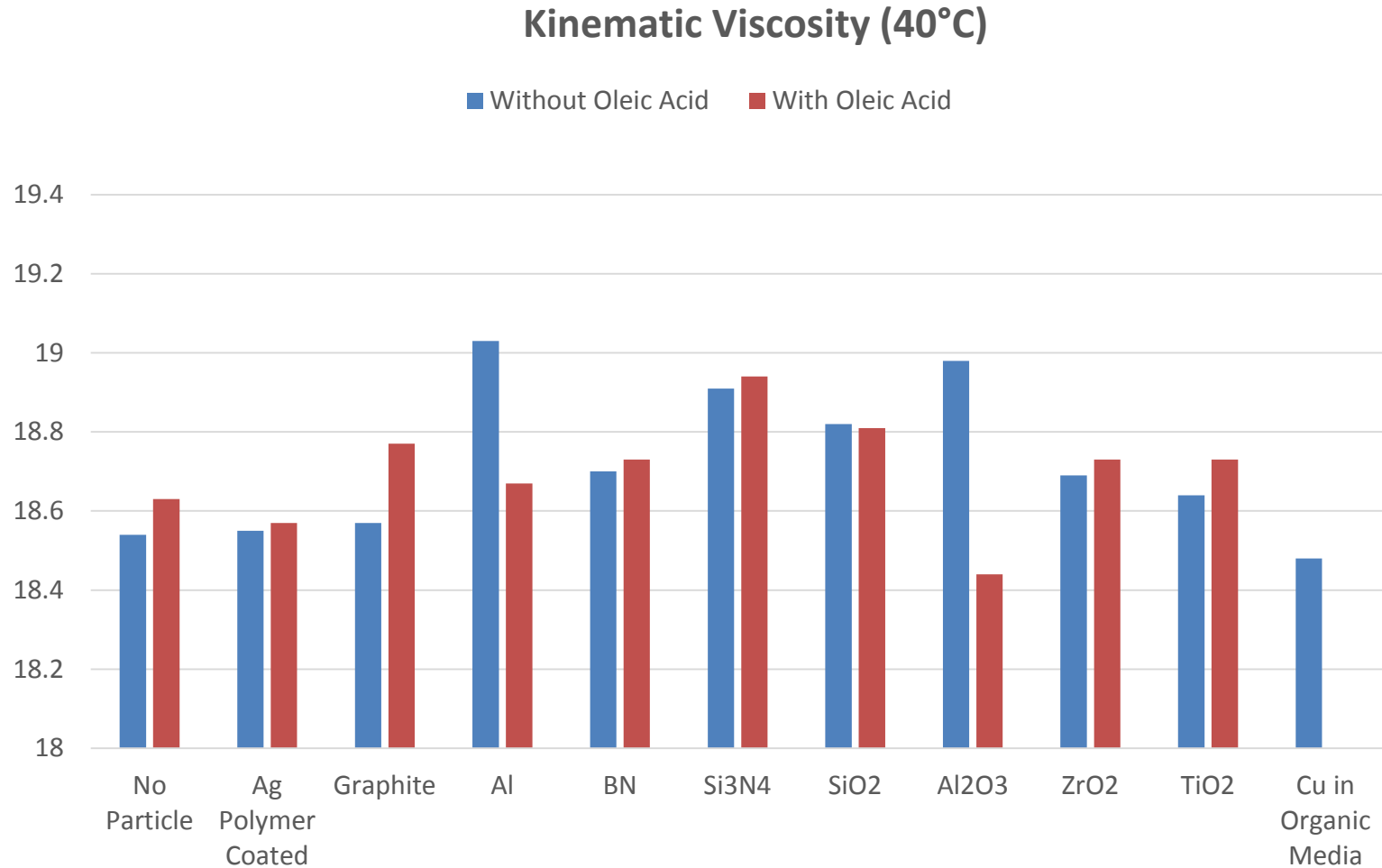
SiO₂



ZrO₂-8Y



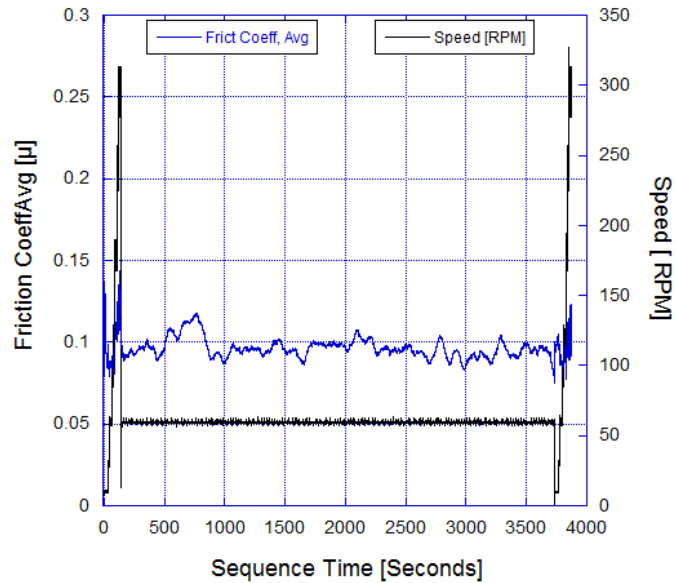
Technical Accomplishment and Progress: Rheological properties- colloidal



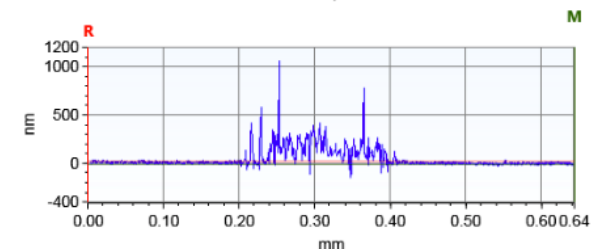
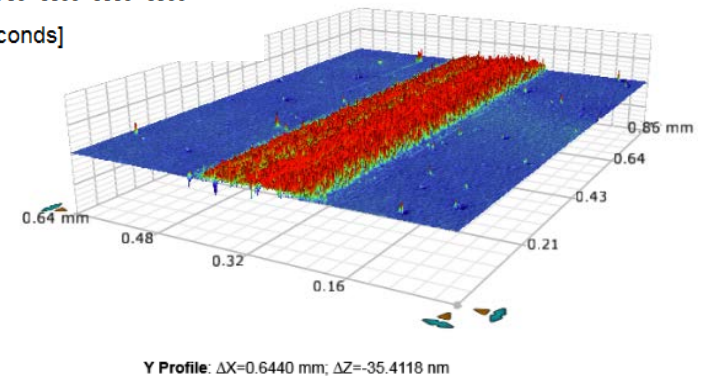
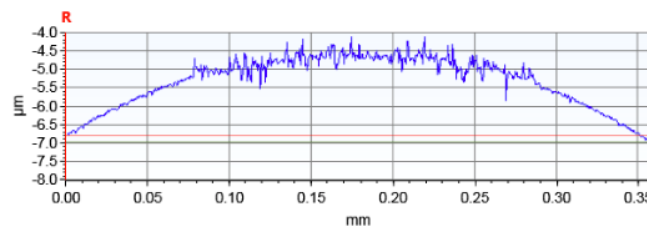
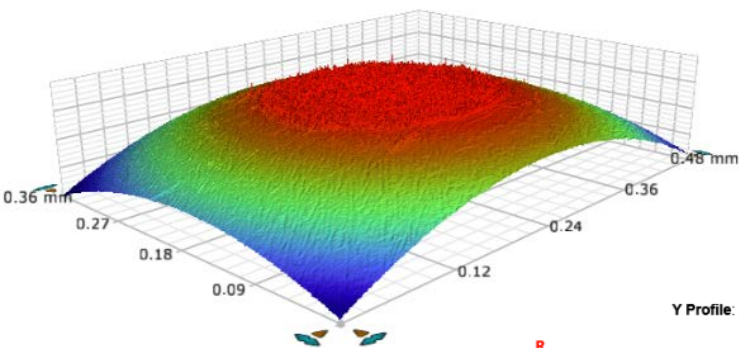
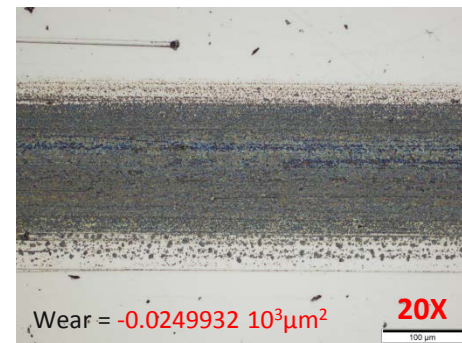
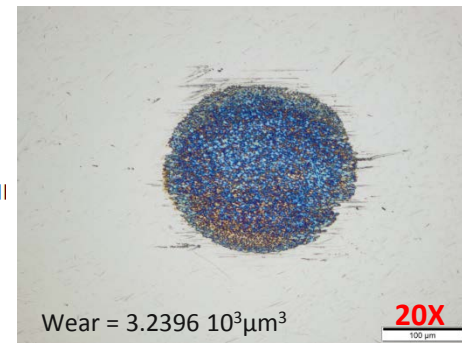
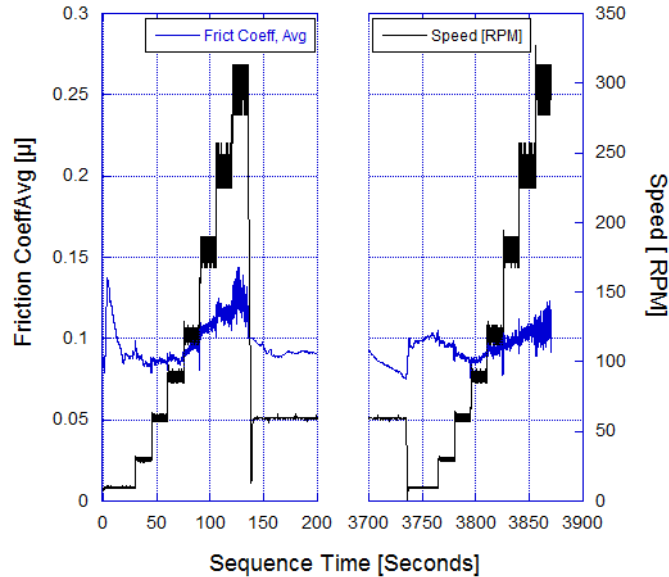
0.1% concentration of particulate additives

Initial friction and wear characterization TiO₂

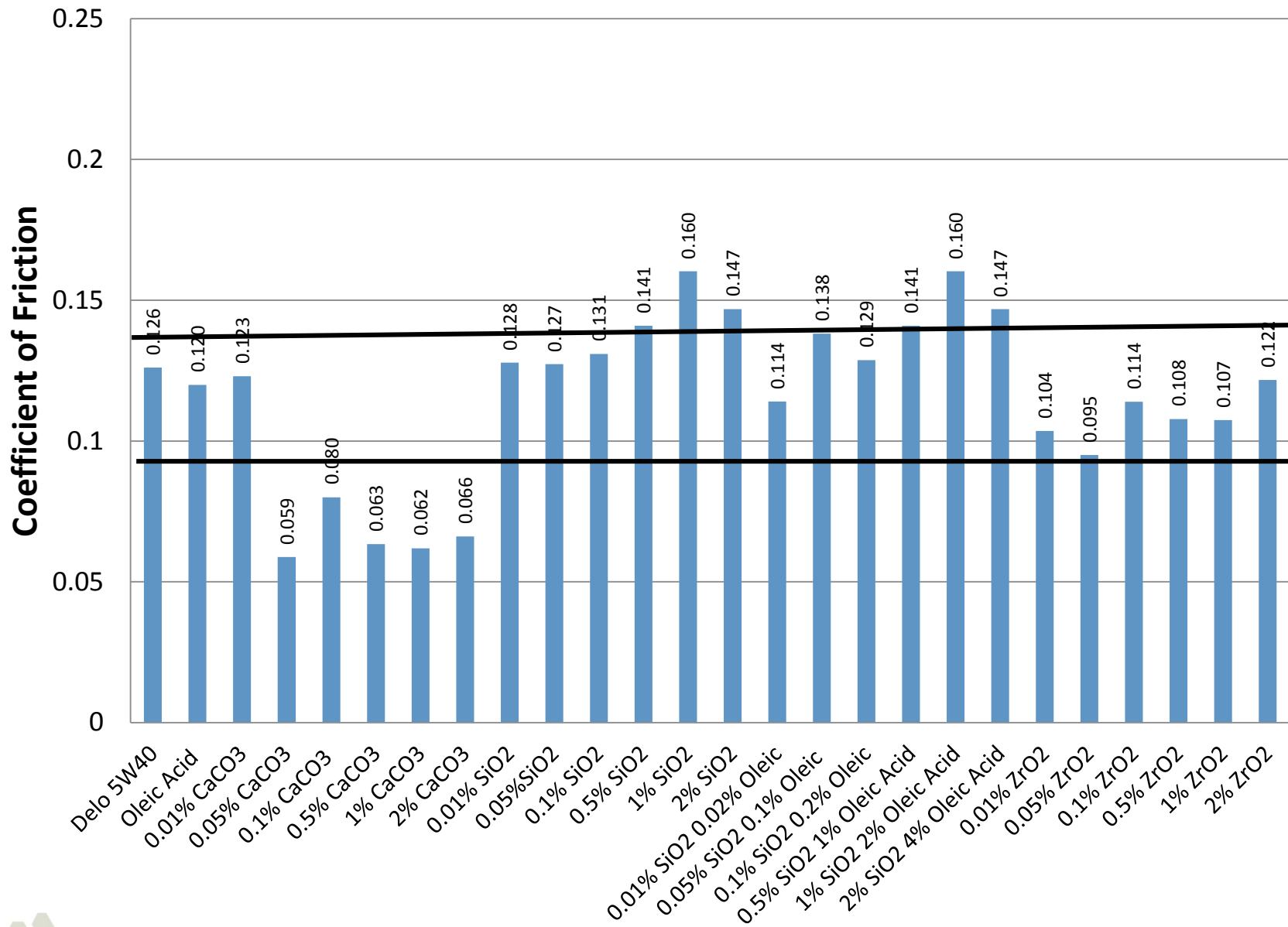
1126a_52100_52100_PAO4+0.01%TiO₂+0.02%OA_5nm_100C_15.6N_1



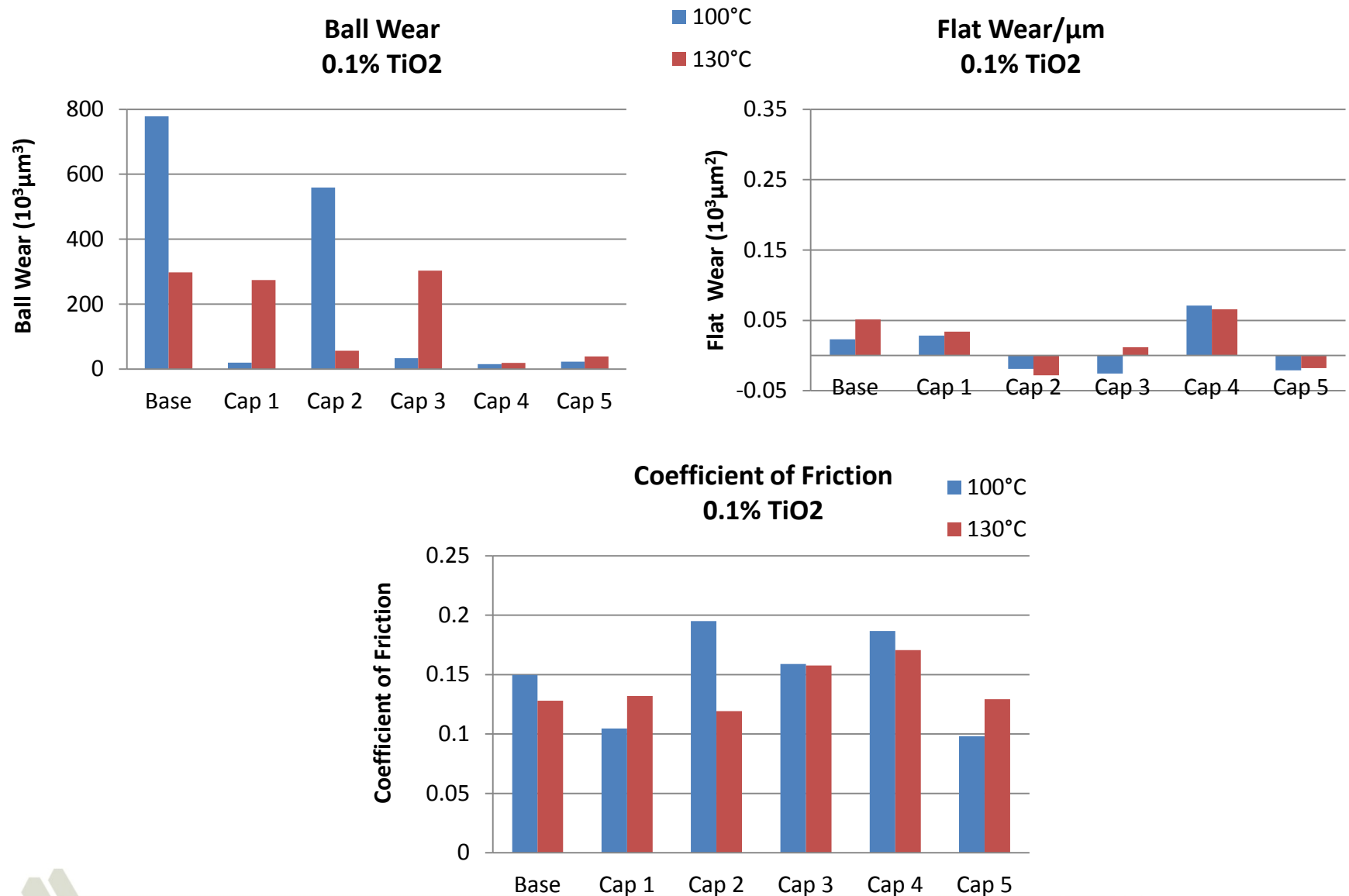
1126a_52100_52100_PAO4+0.01%TiO₂+0.02%OA_5nm_100C_15.6N_1



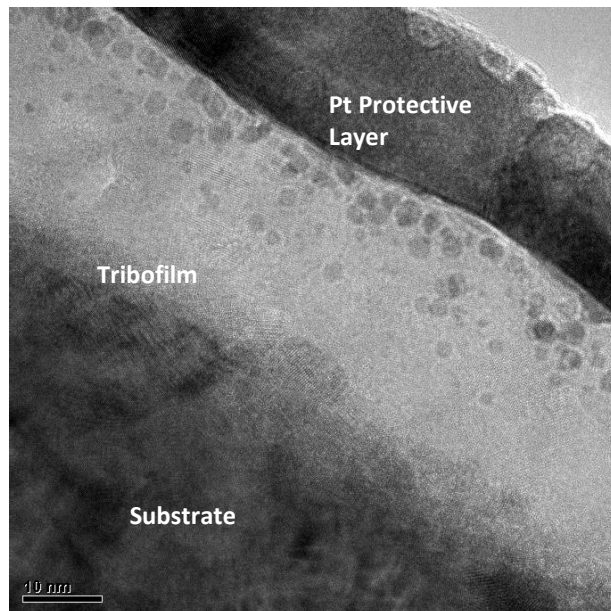
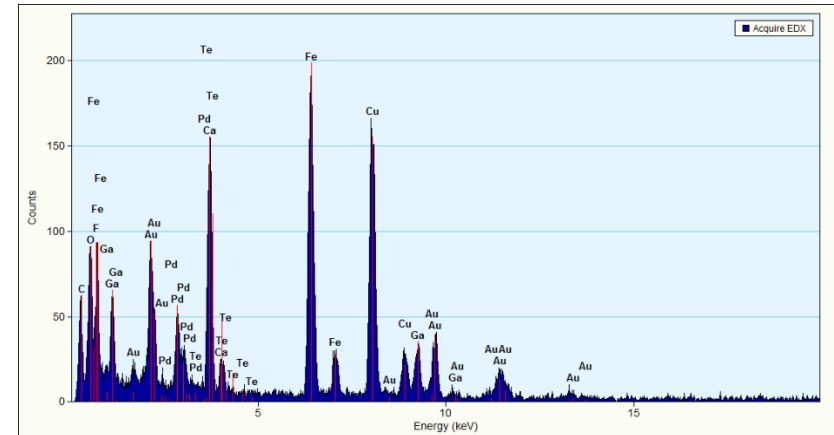
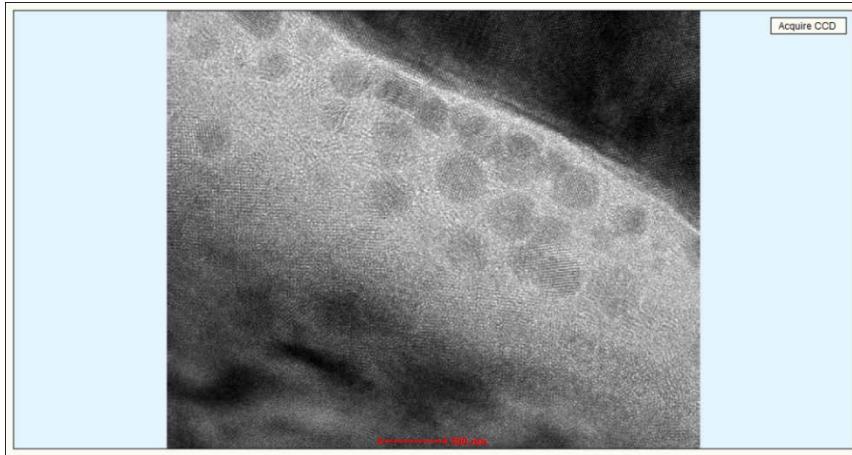
Range of tribological performance for several systems



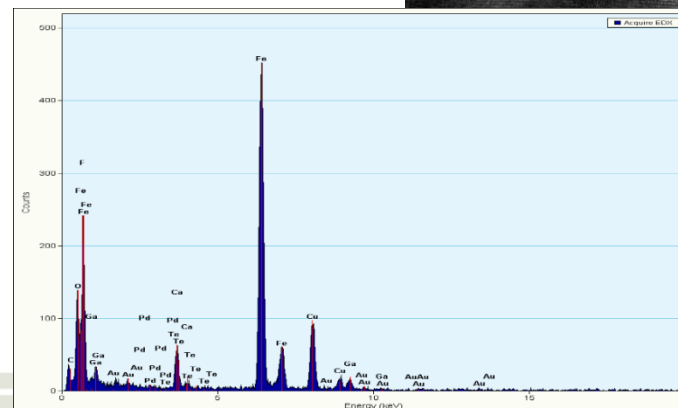
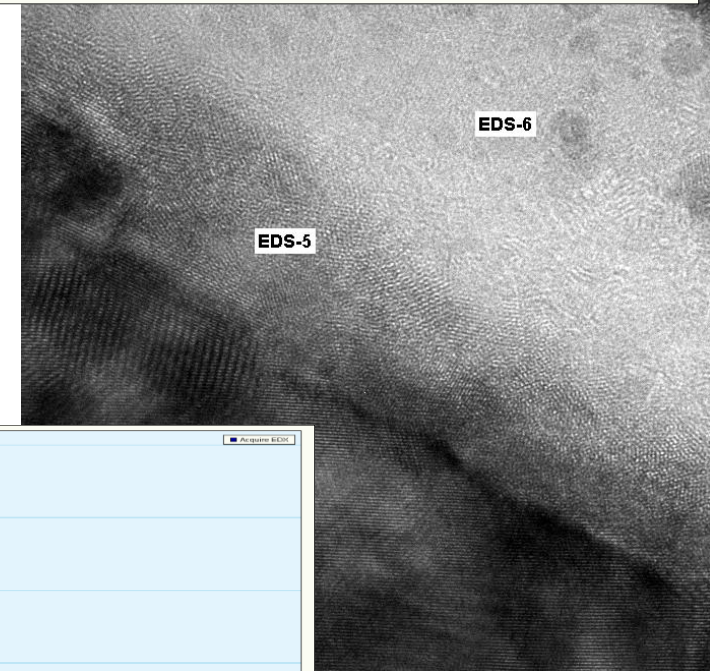
Technical Accomplishment and Progress: - Effect of encapsulator



Tribofilm- preliminary analysis TEM



Tribo films from colloidal additives similar to ones from current advanced lubricants



Summary

- Mixed base fluids all showed superior performance in terms of friction and wear compared to a monolithic PAO fluid under both unidirectional and reciprocating sliding.
 - Attributed to better surface activity of ester as indicated by the formation of protective durable surface films.
 - Thermodynamic modeling of mixed fluid properties underway.
- Identified several candidate materials for colloidal additive system for lubricants.
 - Minimal effect on the viscosity of base fluid – candidate for low viscosity oils.
 - Tribological performance equivalent or superior to nano systems and current advanced lubricants.
- Several effective encapsulation agents identified for the colloidal additive systems.
 - Pathway for optimization of time release behavior.

Future Plans

- Development of thermodynamic model for fluid mixture viscosity and other rheological properties.
- Mechanistic study of tribological performance enhancement for mixed fluids.
 - Characterization of surface films formed during tribological contact.
- Evaluate impact of additives on tribological performance of mixed fluids.
- Tribological performance evaluation of colloidal additives
- Synthesize colloidal particles with different surface layers for different additive functions.
 - Characterize the structure of the optimized layer particles
 - Tribo films by design from colloidal particulate systems
 - Conduct comprehensive tribological performance evaluation
 - Determine the operating lubrication mechanisms and the role of the additives
- Eventual technology transfer to appropriate stake holder.

Project Collaborations - Research activities include collaborations with leading industry and academic partners

■ Consortia Memberships

- Member of the MIT Lubrication Consortium
- Member of the OSU Gear Consortium

■ Collaborations with Industry on Funding Opportunity Announcements (FOAs)

- FOA 239 (Cummins and Lubrizol)
- FOA 793 (Ford, and NWU)
- FOA 991 (Ricardo, Isuzu, ZYNP, Infineum)

■ CRADAs (which have led to focused follow-on projects)

- Ricardo
- Pixelligent
- XG-Sciences

■ Funded Research (business sensitive)

- Vehicle and Engine OEMs
- Suppliers
- Lubricant & Additive OEMs
- Small Businesses (SBIR, STTR)

■ Topics (2-way interactions)

- Failure analysis
- Tribological evaluation (friction and wear)
- Surface characterization
- Friction modeling
- Oil formulation
- Additive formulation
- Coatings
 - DLCs, Fe-Boriding, Nitrides
- Sample/Components for testing
 - Engine blocks
 - Liners, Rings, Pistons
 - Bearings

Technical Backup slides



Prediction of viscosity of mixed fluids

A model developed based on Eyring's absolute rate theory approach and the UNIQUAC equations

Eyring's rate theory

$$\eta = \frac{hN}{v} \exp\left(\frac{\Delta g^\ddagger}{RT}\right) \quad (1)$$

A correction/excess term is added to account for non-ideal behavior

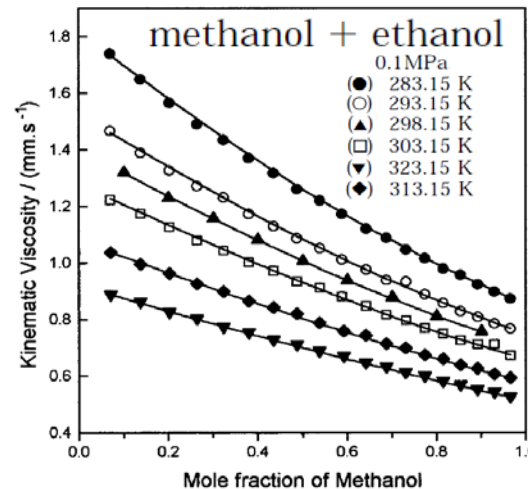
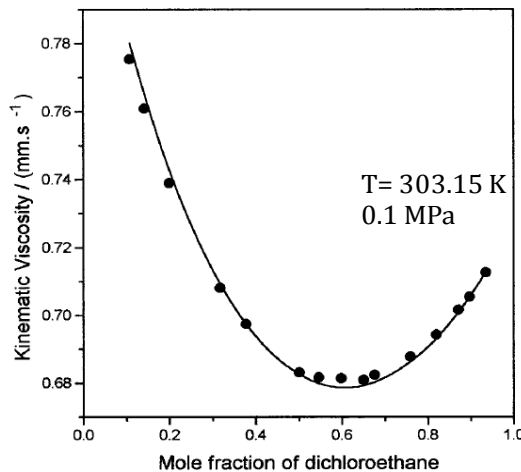
$$\Delta g^\ddagger = \Delta g_{\text{ideal}}^\ddagger + g_E^\ddagger \quad (2)$$

$$\frac{\Delta g_{\text{ideal}}^\ddagger}{RT} = \sum_i x_i \ln(\eta_i v_i^0) - \ln(hN) \quad (3)$$

$$\frac{g_E}{RT} = \sum_{i=1}^{N_{\text{SOL}}} x_i \ln\left(\frac{\phi_i}{x_i}\right) + \frac{z}{2} \sum_{i=1}^{N_{\text{SOL}}} q_i x_i \ln\left(\frac{\theta_i}{\phi_i}\right) - \sum_{i=1}^{N_{\text{SOL}}} x_i q_i \ln\left(\sum_{k=1}^{N_{\text{SOL}}} \theta_i \psi_{ki}\right) \quad (4)$$

UNIQUAC Model

This model has been applied to several hundred binary mixtures



v_i^0 = molar volume of pure liquid i
 x_i = mole fraction of component i
 z = coordination number
 N_{SOL} = number of solvents in the mixture
 q_i = surface area parameter
 θ_i = surface area fraction
 ϕ_i = volume fraction
 ψ_{ki} = UNIQUAC interaction parameter between species k and i
 i = pure component i

Table of colloidal systems being explored

Nanoparticle	Size	Purity	Comments (Shape, coatings etc.)
SiO ₂	5-15 nm	99.8%	Surface modified, hydrophobic and oleophilic
TiO ₂	5-10nm	99.5%	Rutile, Silane Coated
ZrO ₂ -8Y	20nm	Y ₂ O ₃ -13.5%, ZrO ₂ -86%	Near spherical morphology
Al ₂ O ₃	5nm	99.9%	Gamma, Fibrous morphology
Si ₃ N ₄	20nm	99%	Amorphous
Poly Coated Ag	15nm	99.9% of Ag Composition: 25% Ag+75% Polymer	Self dispersible
Al	18nm	99.9%	Spherical morphology
Graphite	3-4nm	93%	Spherical Morphology, hexagonal carbon
BN White	10nm		
Cu in Organic Media	5-7nm	14% Cu	Oil soluble, dispersible, Lubricants Additive